BOOSTER HIGH EXPLOSIVES. Booster high explosives are materials that are insensitive to both mechanical shock and flame but that explode with great violence when set off by an explosive shock, such as that obtained by detonating a small amount of a primary explosive in contact with the high explosive. They are thus energy amplifiers. Decomposition proceeds by means of detonation, which is rapid chemical rupturing of bonds progressing directly through the mass of the explosive. Detonation is thought to be a chain reaction and proceeds at rates of around 6000 m/s. It is this high rate of energy release, rather than the total energy given off, that makes a product an explosive. Nitroglycerine has only one-eighth the energy of an equivalent weight of gasoline. On the other hand, most explosives, when unconfined and unshocked, will merely burn if ignited.

Important boosters are RDX (cyclotrimethylenetrinitramine), PETN (pentaerythritol-tetranitrate), and Tetryl (2,4,6-trinitrophenyl methyl nitramine). There are also some heat-resistant boosters, e.g., HMX (cyclotetramethylenetetranitramine).

BLASTING AGENTS. Blasting agents are powerful explosive agents that meet the criterion that they cannot be detonated by means of a No. 8 blasting cap when unconfined. They are, therefore, very safe to handle. A powerful booster is needed to start detonation.

SLURRY EXPLOSIVES. Slurry explosives are ammonium nitrate mixtures which frequently contain another oxidizer as well as a fuel dispersed in a fluid medium which, among other functions, controls the rheology of the gel-slurry.

EXPLOSIVE CHARACTERISTICS

Some very interesting technology has been used to determine the characteristics of explosives. Much is empirical, but measurements of heat values, rates of combustion and detonation, shattering ability, sensitivity, etc., reflect modern instrumental application to high-speed phenomena, and the results are a tribute to the skill and technology of explosives scientists and technicians.

Tests for sensitivity to impact and heat, stability on storage, shattering ability (brisance), explosive strength per unit weight, volatility, solubility, density, hygroscopicity, compatibility with other explosives, additives and possible metals used for enclosures, resistance to hydrolysis, and toxicity must all be run in a standard manner and taken into consideration.

The brisance of an explosive is measured by exploding a measured quantity of it in a sand bomb, a heavy walled vessel filled with a standard coarse sand which is crushed by the explosion. Screening measures the sand crushed, and from this the explosive force. Another test of a somewhat similar nature is the Trauzl block test. This test measures the strength of the explosive by measuring the ballooning of a soft lead cylinder in which the explosive is inserted and exploded. Results are reported in terms of the increase in volume, expressed in cubic centimeters, caused by the detonation of the explosive. Brisance is probably a combination of strength and velocity. Cook states that there is no reason to believe that brisance is power; it seems to be directly related to detonation pressure.[2]

The sensitivity of an explosive to impact[3] is determined by finding the height from which a standard weight must be allowed to fall in order to detonate the explosive.

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[2]Cook, op. cit., p. 271.

[3]Macek, Sensitivity of Explosives, *Chem. Rev.* 62, 41 (1962) (140 references).

It is important that explosives for use in mines, particularly coal mines, be of such a type that on explosion they evolve less than the specified amount of allowable toxic gases, as determined or specified by federal or state regulating agencies, and produce a minimum of flame. This latter requirement assures that the explosive is incapable of igniting mixtures of air and coal dust, or air and methane (the so-called fire damp), which inevitably occur in coal mines. Explosives for mine use are tested and their properties specified by the Bureau of Mines; they are commonly known as permissibles. Permissibles differ from other explosives, particularly black powder, most markedly in the fact that they produce a flame of small size and extremely short duration. Permissibles contain coolants to regulate the temperature of their flame, further reducing the possibility of igniting several types of combustible mixtures. Table 22.2 shows the characteristics of explosives.

INDUSTRIAL EXPLOSIVES

Cost per unit of work done (shattering of material or displacement without shattering) is almost as important as safety for industrial explosives. Present agents are less expensive and far safer than their predecessors.

HISTORICAL. Black powder has been the preferred blasting agent because it is less shattering in its effects. It is an intimate mixture of KNO_3, sulfur, and charcoal in the approximate proportions of 75:15:10. About 50 percent of the products of combustion are solids, giving its flames great igniting power, which is undesirable where combustible gases or solids are present but useful for igniting propellants.

Starting in 1860, dynamite dominated the blasting industry for a century, but its current use is small and diminishing.

BLASTING AGENTS AND SLURRY EXPLOSIVES. Blasting agents and slurry explosives have become the principal industrial explosives because they may be handled by simple machinery almost completely without danger and because their cost is very low. These are usually ammonium nitrate mixtures sensitized with nonexplosive fuels such as oil or wax. Properly initiated, such mixtures produce energies surpassing that of dynamite and are far cheaper. Ammonium nitrate is the world's most widely used explosive substance.

Cook lists the types and compositions of present-day industrial explosives (see also Table 6.3). Explosives play such a vital part in the nation's economy that their consumption has been suggested as a reliable index of the general scientific and technical atmosphere. See Table 6.4 for U.S. consumption of explosives in the mineral industry. The current energy crisis may well stimulate the use of explosives, particularly in mining coal and low-grade domestic ores.

NITROGLYCERIN AND DYNAMITE. Nitroglycerin was the first high explosive to be employed on a large scale. Nitration is effected by slowly adding glycerol of high purity (99.9% +) to a mixture having the approximate composition: H_2SO_4, 59.5%, HNO_3, 40%, and H_2O, 0.5%. Nitration is accomplished in 60 to 90 min in agitated nitrators equipped with steel cooling coils carrying brine[4] at 5°C to maintain the temperature below 10°C. After nitration, the

[4]Brine can be a little cooler than 5°C, but pure nitroglycerin freezes at 12.8°C. Freezing would be hazardous, since it might interfere with the temperature control.

Table 6.2 Summary of Characteristics of Explosives

Name	Formula	Products per Formula Weight	Q_v, J/kg	T_e, °C	f, kg/cm^2	V, m/s	Trauzl Expansion, cc/10 g	Potential, $\times 10^5$ kg-m
Gunpowder	$2KNO_3 + 3C + S$	$N_2 + 3CO_2 + K_2S$	2098	2090	2,970	—	30	2.1
Nitrocellulose	$C_{24}H_{29}O_9(NO_3)_{11}$	$20.5CO + 3.5CO_2 + 14.5H_2O + 5.5N_2$	5234	2800	10,000	6100	420	5.3
Nitroglycerin	$C_3H_5(NO_3)_3$	$3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$	6389	3360	9,835	8500	590	6.5
Ammonium nitrate	NH_4NO_3	$2H_2O + N_2 + 0.5O_2$	1608	1100	5,100	4100	300	1.6
TNT	$C_7H_5(NO_2)_3$	$6CO + C + 2.5H_2 + 1.5N_2$	2747	2200	8,386	6800	260	2.8
Picric acid	$C_6H_2(OH)(NO_2)_3$	$6CO + H_2O + 0.5H_2 + 1.5N_2$	3546	2717	9,960	7000	300	3.6
Ammonium picrate	$C_6H_2(NO_2)_3ONH_4$	$6CO + H_2O + 2H_2 + 2N_2$	2604	1979	8,537	6500	230	2.6
Tetryl	$C_7H_5N_5O_8$	$7CO + H_2O + 1.5H_2 + 2.5N_2$	3802	2781	10,830	7229	320	3.9
Mercury fulminate	$Hg(ONC)_2$	$Hg + 2CO + N_2$	1759	4105	5,212	3920	213	1.8
Lead azide	PbN_6	$Pb + 3N_2$	2864	3180	8,070	5000	250	2.9

SOURCE: After Meyer, *Science of Explosives*, Crowell, New York, 1943; for more recent investigations of characteristics of explosives, cf., Cook, *Science of High Explosives*, ACS Monograph 139, Reinhold, New York, 1958, p. 284, table 12.1; a more extensive list will be found in Riegel, *Industrial Chemistry*, 7th ed., Reinhold, New York, 1974, pp. 570–596.

NOTE: Q_v = heat of explosion at constant volume (small in comparison with fuels, but explosives exert their energy rapidly); T_e = explosion temperature, f = specific pressure, i.e., exerted by 1 kg in a volume of 1 L at T_e heat; V = velocity of detonation wave (currently measured by high-speed photography).

***Table* 6.3** Classes of Well-Characterized Slurry Explosives and Slurry Blasting Agents

Designation*	% Sensitizer	Oxidizer†	Water, %	
			Nominal	Range
SE-TNT	17–60 TNT	AN, SN, BN, SC, NaP, C	15	8–40
SE-CB	15–35 CB	AN, SN, C	15	12–16
SE-SP	20–60 SP	AN, SN, BN, SC, NaP, C	15	2–20‡
SE-HSSP	20–60 HSSP	AN, SN, C	15	2–20‡
SE-TNT/Al	5–25/0.5–40 TNT/Al	AN, SN, NaP, C	15	10–30
SE-SP/Al	10–25/1–40 SP/Al	AN, SN, C	15	12–30
SBA-Al	0.1–40 Al 0–12 fuel	AN, AN/SN, AN/NaP, NaP	15	6–30‡
SBA-fuel	4.0–15 solid fuel	AN, AN/SN, NaP, SC	15	3–16‡

*TNT, trinitrotoluene, CB, composition B; SP, smokeless powder; HSSP, high-strength smokeless powder; fuel, various types—sulfur, gilsonite, other solid hydrocarbons, NH_4-lignosulfonate, others.

†AN, ammonium nitrate; SN, sodium nitrate; BN, barium nitrate; NaP, sodium perchlorate; SC, sodium chlorate; C, combinations (AN/SC incompatible).

‡Low percent requires water extenders, such as formamide, ethylene glycol, sugar, molasses.

SOURCE: *Ind. Eng. Chem* 60(7) 44 (1968). Reprinted with permission of the American Chemical Society.

mixture of nitroglycerin and spent acid is allowed to flow through a trough (a trough is easier to clean completely than a pipe) into separating and settling tanks some distance from the nitrator. The nitroglycerin is carefully separated from the acid and sent to the wash tank, where it is washed twice with warm water and with a 2% sodium carbonate solution to ensure the complete removal of any remaining acid. Additional washes with warm water are continued until no trace of alkalinity remains. See Fig. 6.1, where the quantities of raw material are also listed. The product is really glyceryl trinitrate, and the reaction is an esterification.

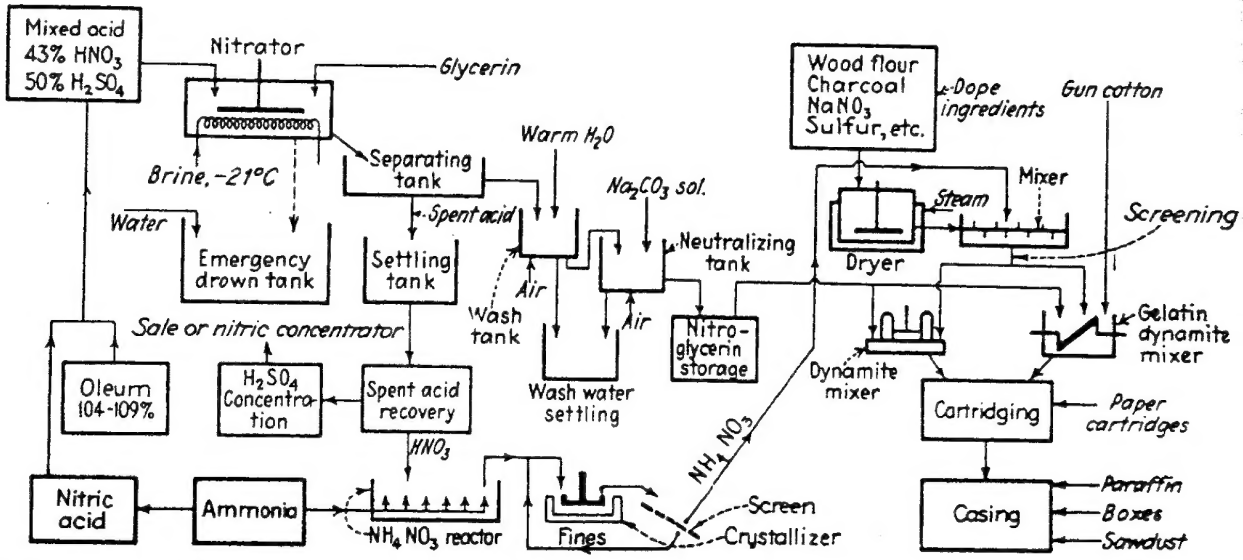
Small continuous stirred stainless-steel nitrators (Biazzi and other types) give higher yields, lower operating costs, and greater safety than the batch process illustrated in Fig. 6.1 because much less material is in process at any given time and control is easier. Most of the streams are in the form of emulsions, an inherently safer state. Other glycol nitrates are also made in continuous nitrators.

Nitroglycerin is a liquid similar in appearance to the original glycerol. It is sensitive to blows and freezes at 13°C; when solid it is less sensitive. The solid tends to explode incompletely, so frozen nitroglycerin must always be thawed before using. To make nitroglycerin

***Table* 6.4** U.S. Distribution of Consumption of Explosives in the Mineral Industry*
(Includes Coal Mining, Metal Mining, Quarrying, and Nonmineral Mining)

	1977	1978	1979	1980
Ammonium nitrate–fuel oil, mixed and unprocessed, %	85.5	83.9	83.8	85.9
Water gels and slurries, %	8.9	11.6	12.0	9.9
Other high explosives, %	4.0	3.4	2.9	2.7
Permissible explosives %	1.6	1.0	1.3	1.4
Total, thousands of metric tons	1392	1522	1587	1676

*Calculated from data in the *Minerals Yearbook, 1982*.



In order to produce 1 t of nitroglycerine, the following materials and utilities are required:

HNO_3 (100%)	1000 kg (10% recovered)	Refrigeration	1.5 t ice equivalent
H_2SO_4 (100%)	1000 kg (96% recovered)	Direct labor	5 work-h
Glycerin	430 kg		

Fig. 6 .1. Flowchart for the manufacture of nitroglycerin and dynamites. Usually an evaporator is needed between the ammonium nitrate reactor and the crystallizer.

safer and easier to handle, it is usually manufactured into dynamite. Dynamite was originally made by absorbing nitroglycerin into kieselguhr, a kind of clay. Modern dynamites generally use wood flour, ammonium nitrate, or sodium nitrate to absorb the nitroglycerin. Such a mixture is easy to handle and can be made to contain as much as 75% nitroglycerin and yet retain its solid form. Because of the demand for a nonfreezing dynamite for use in cold weather, dynamites containing other materials designed to lower the freezing point of the mixture are used, for example, glycol dinitrate. Such nonfreezing dynamites have potentials as great as "straight" dynamite. Nitrocellulose can be gelatinized by nitroglycerin, and the resultant firm gel is commonly known as gelatin dynamite. The ability to act as a combination plasticizer and explosive makes nitroglycerin and the similar diethylene glycol dinitrate (DEGN) useful in plastic explosives and smokeless powder manufacture. Almost without exception the nitro compounds and nitric acid esters used as explosives are toxic. The degree of toxicity varies widely with the material in question, but most are capable of causing acute distress if taken orally. Nitroglycerin has a small medical use as a vasodilator. Extremely toxic properties would weigh heavily against any new explosive that might be introduced.

PROPELLANTS, ROCKETS, AND MISSILES

PROPELLANTS FOR GUNS. The oldest propellant known is black powder, but its use today is trivial. It burns badly and far too fast for propellant use if the ingredients are left in finely divided form. Merely stirring the ingredients together produces useless material. Larger

grains are produced by intimate, intensive mixing, the mix actually being made into a dense colloid in a heavy-duty mixer. Black powder remains the best igniter available.

Smokeless powder replaced black powder for several reasons, its smokelessness, its superior power, and its better storage characteristics, but principally because it can be formed into stable grains whose size and shape governs the burning characteristics. This makes possible the construction of large rockets and guns. Smokeless powder is colloided cellulose nitrate, usually containing a plasticizer, such as nitroglycerin or nitroglycol. Sometimes a nonexplosive plasticizer such as dibutyl phthalate is added and usually about 1% of diphenylamine or similar amine designed to improve its storage life. When the only explosive used is nitrocellulose of over 13% nitrogen content, it is known as single-base powder; when two or more explosive ingredients are used (nitrocellulose and nitroglycerin), the grains are less brittle and the product is known as a double-base powder. Most sporting ammunition uses double-base powder. Military powders with grains over 25 mm in diameter are used in large rifles. Combustion of smokeless powder proceeds at a relatively constant rate in layers parallel to the ignited surface, so the speed of gas evolution (hence maximum bore pressure) is controlled by the geometry of the grain. Most rifle grains have internal perforations to control burning rates so as to be progressive bore pressure (increasing with time), neutral (constant with time), or degressive (decreasing with time).

NITROCELLULOSE.[5] The explosive properties of nitrated cotton were recognized at an early date. The discovery of methods for converting the material into a dense uniform colloidal mass reduced the surface and the rapidity of the explosion. With the discovery of suitable stabilization methods to prolong its storage life, nitrocellulose soon put black powder out of use as a propellant. Most nitrocellulose is now made from wood fibers rather than cotton.

The cellulose molecule is a complicated one, with a molecular weight frequently as high as 300,000. Any given sample of cellulose contains a wide distribution of molecules, all having the empirical formula $[C_6H_7O_2(OH)_3]_n$. There are thus three hydroxyl groups per fundamental (glucose) unit that may be esterified with nitric acid to yield a theoretical nitrogen content of 14%, which is higher than any commercially used product. The reaction is

$$C_6H\text{-}O_2(OH)_3 + 3HONO_2 + (H_2SO_4) \rightarrow C_6H\text{-}O_2(ONO_2)_3 + 3H_2O + (H_2SO_4)$$

Celluloses that have not been nitrated completely to the trinitrate are used as various industrial cellulose nitrates as shown in Fig. 6.2. In addition to nitrate esters, some sulfate esters are formed by sulfuric acid, which must be used to tie up the water resulting from the nitration reaction and to permit the reaction to progress to the right. These sulfate esters are unstable, and their decomposition would give rise to a dangerous acid condition in the stored powder if not removed; they are decomposed in the poaching process.

The finished nitrocellulose should not be allowed to become acid in use or in storage, since this catalyzes its further decomposition. A stabilizer is therefore added which reacts with any trace of nitrous, nitric, or sulfuric acid that may be released because of the decomposition of the nitrocellulose and thus stop further decomposition. Diphenylamine is used for smokeless powder (diphenylurea in Great Britain), and for celluloid, urea. The diphenylamine forms a series of innocuous compounds with the evolved gases.

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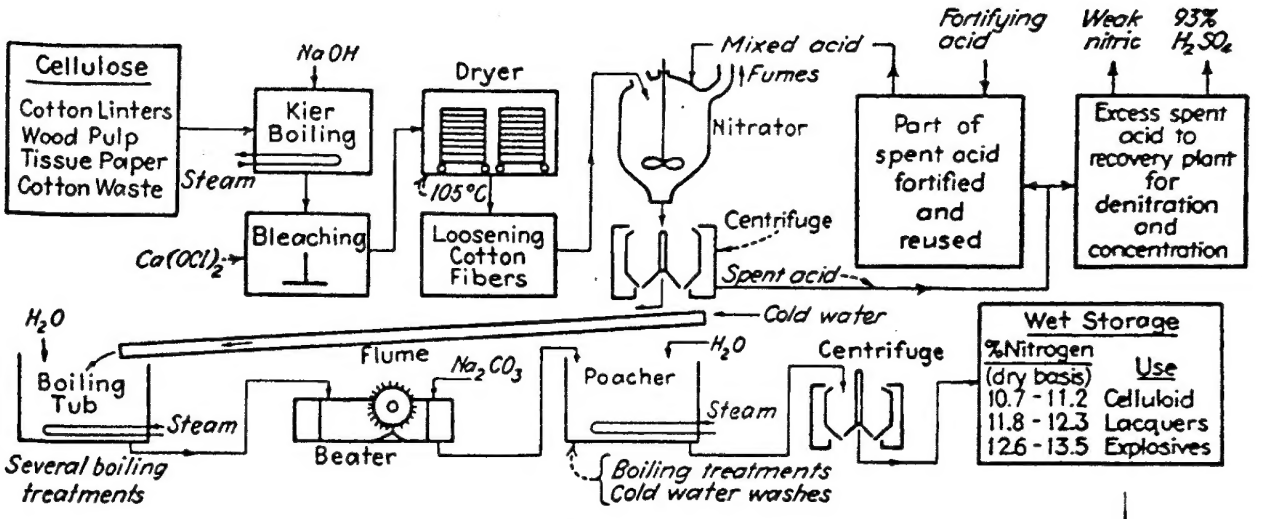
[5]Although the word "nitrocellulose" is commonly used for nitrated cellulose fiber, the material is not a nitro compound but a true ester of nitric acid. The name cellulose nitrate is therefore chemically more proper, but nitrocellulose is more widely employed in the industry.



In order to produce 2.2 kg of dry cellulose nitrate (0.75 kg raw cotton furnishes about 0.6 kg of purified cotton fibers), the following materials and utilities are required:

Cotton linters	0.75 kg	Chlorine	Variable but small
HNO_3 (100%)	1.0 kg	Water	227 L
H_2SO_4 (100%)	0.5 kg	Direct labor	0.03 work-h
Na_2CO_3	0.002 kg		

Fig. 6 .2. Flowchart for cellulose nitrate (nitrocellulose) manufacture. NOTE: Nitrogen content of cellulose nitrate is controlled by the composition of nitration mixed acid. Quality product depends on the grade of cellulose used and the care devoted to manufacturing procedures. Steps shown are for the military product. In use, wet product is dried by alcohol displacement.

The commercial manufacture of cellulose nitrate is illustrated in Fig. 6 .2 with the following steps:

Cotton linters, or wood pulp high in α-cellulose, are purified by boiling in Kiers (vats) with dilute caustic soda solution.

Bleaching is effected with CaClOCl, NaOCl, or $Ca(OCl)_2$.

The cotton is dried, fluffed, and weighed.

Mixed acid is made up from fortifying acid and spent acid, brought to proper temperature and run into the nitrator.

Nitration (esterification) is usually conducted under carefully controlled conditions in a "mechanical dipper" nitrator.

One nitrator charge is formed by 14.5 kg of purified cellulose. The cellulose is agitated with approximately 682 kg of mixed acid at 30°C for about 25 min. The composition of the acid used averages: HNO_3, 21%; H_2SO_4, 63%; N_2O_4, 0.5%; H_2O, 15.5%.

The entire nitrator charge is dropped into a centrifuge, where the spent acid is centrifuged from the nitrated cellulose.

The spent acid is partly fortified for reuse and partly sold or otherwise disposed of, e.g., by denitration and concentration of the H_2SO_4.

The nitrated cellulose is drowned with water, washed by boiling, and again washed in a beater.

In order to produce a smokeless powder that is more stable on storage, the following purification is employed to destroy unstable sulfate esters and to remove free acid completely. (This is a military procedure; commercially, the nitrated cellulose is dissolved in a solvent and neutralized chemically; this procedure works well and gives a stable product.)

Forty hours of boiling with at least four changes of water is followed by pulping of the fiber by means of a beater.

Poaching of the washed nitrated cotton by boiling first with a dilute Na_2CO_3 solution (2.5 kg of soda ash per metric ton of cellulose nitrate) and then many washes of boiling water.

The poached nitrocellulose is freed of most of its water by centrifugation. The water content is now approximately 28%.

At this point the nitrocellulose is usually stored and a laboratory examination made.

The water content of the nitrated cotton is reduced to a low figure by alcohol displacement of the water.

The nitrated cellulose is broken up and made into a dense colloid by mixing with alcohol, ether, diphenylamine, and other modifying agents.

Grains are formed by extrusion through dies, and these are dried and blended to form smokeless powder grains. The commonest shape is a pierced cylinder (macaroni) for small arms and a multiply pierced cylinder or rosette for larger guns.

The cellulose produced in this manner contains about 12.6% nitrogen and is known as pyrocotton. By using a stronger acid, the nitrogen content may be made as high as 13.6%. Cotton nitrated to contain 13.2% nitrogen or greater is known as guncotton. Modern military smokeless powder contains about 13.15% nitrogen and is made from a blend of pyro- and guncotton.

Smokeless powder is dense colloidal nitrocellulose containing about 1% diphenylamine and a small amount of a plasticizer such as dibutyl phthalate. The manufacture is shown in Fig. 6.3.

An interesting variant on this manufacturing process produces spheres, known as ball powder. The nitrocellulose, along with the additives, is dissolved in a solvent, e.g., mixed ketones, to form a lacquer which is then carefully emulsified with water. The emulsion is then inverted

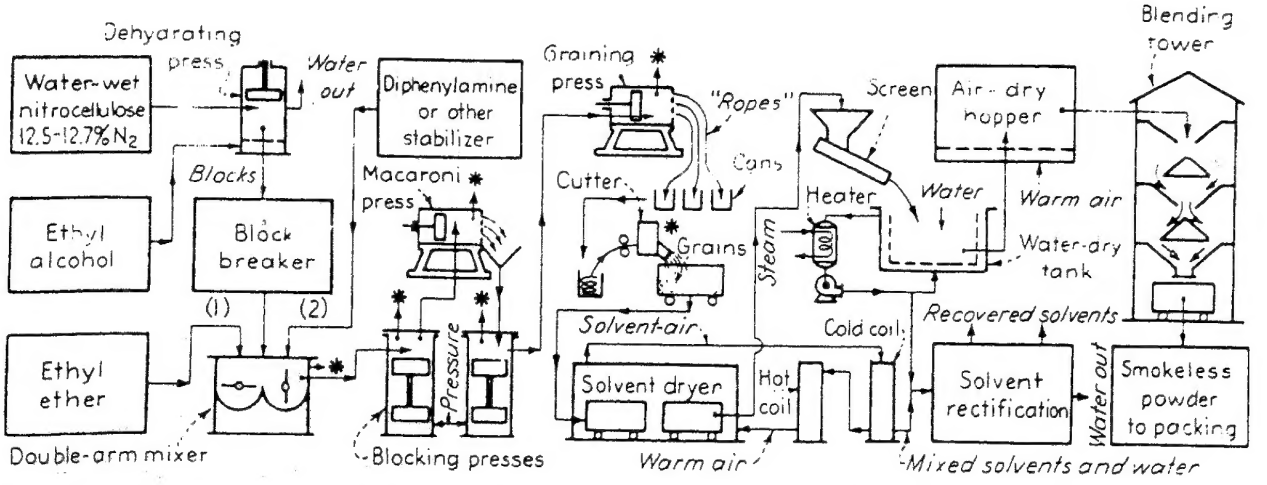


Fig. 6.3. Flowchart for single-base smokeless powder manufacture. For a flow sheet for nitrocellulose manufacture, see Fig. 6.2. NOTE: Asterisks denote equipment connected to solvent recovery system.

to give small spheres, and the solvent is driven off with heat. These spheres are sieved to give uniform size and can have nitroglycerine added to them to give double-base plasticized balls. Treatment with burning-rate regulators, such as dinitrotoluene, can cause the rate of burning to increase as the surface area for burning decreases. A sphere is the most degressive-burning shape possible. Proper treatment results in a progressive burning ball. Balls much above 3 mm are not practical, so only ammunition up to 50 caliber (0.5 in = 12.7 mm bullet diameter) is made. Much sporting ammunition is ball powder.

PROPELLANTS FOR ROCKETS

There are a great variety of choices in the design of efficient propulsion systems; liquids, solids, and castable solid units are all in use. Rocket propulsion systems derive their energy from chemical sources.

Rocket propellants[6] are low explosives which consist of fuels which include their own oxidant or other reactant necessary to cause the planned reaction. The thrust of the escaping hot gases pushes the device forward, according to the principle that forces act equally in opposite directions. High-performance systems under fine control are used for the launching of missiles and spacecraft for exploratory and scientific missions and for military offense and defense. Careful selection of the propellant ingredients is important to give high chamber temperature and pressure. The gases produced should be of low molecular weight. The reaction temperature may be so high that resistant structural materials are not available, in which case the temperature must be reduced. The fuel should be one which provides the greatest amount of heat for the smallest amount of weight. The foregoing factors are the most important ones in the equation defining *specific impulse*, or pounds of thrust per pound of weight of propellant burned per second, wherein the square root of the absolute temperature T divided by the square root of the average molecular weight M of the exhaust gases determines the value of the specific impulse: S. I. $= \sqrt{T}/\sqrt{M}$. Figure 6.4 shows the characteristics of major rocket propellants.

LIQUID PROPELLANTS.[7] Liquid propellants are those added to the combustion chamber as liquids. This includes all liquids used in a single propellant system, serving as fuel, oxidizer, and catalyst. Liquid fuels are, for the most part, used in bipropellant systems (fuel and oxidizer stored in two fuel tanks and fed separately to the combustion chamber). Monopropellants combine the fuel and oxidizer in one mixture. A few of the better-known liquid propellants are listed in Table 6.5, together with some of their characteristics. Liquid propulsion systems are the means for achieving the propulsive energy required for human space travel.

Large high-performance rockets now use LOX (liquid oxygen) and LH_2 (liquid hydrogen) propellants, because of their high specific impulse and low cost. Greater storage efficiency is achieved by catalytic conversion of nearly all the hydrogen to the para form. Large solid units are used where long storage time is required.

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[6]Tschinkel, Propellants for Rockets, *Chem. Eng. News* 32 (26) 2582 (1954) (excellent article with equations and tables); ECT, 3d ed. vol. 9, 1980, p. 620; Penner, Combustion and Propulsion Research, *Chem. Eng. News* 41 (2) 74 (1963).

[7]Kit, *Rocket Propellant Handbook*, Macmillan, New York, 1960.